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### Heat exchanger

The invention relates to a heat exchanger with surface-treated heat transfer surfaces. It also relates to a process for the surface treatment of heat exchangers.

To satisfy industry demands imposed on components, for example those imposed by the automotive industry on heat exchangers, it is in many cases imperative that the material surfaces be treated. A surface treatment is intended to provide the associated components with specific properties which protect them in particular from environmental influences so as to achieve improved performance and a longer service life. In this context, in particular the specific application area and structural conditions need to be taken into account.

Heat exchangers, in particular evaporators, which are used in air-conditioning systems - in particular in motor vehicles - usually comprise a plurality of disks or tubes which are arranged in a row, are connected to one another in a fluid-tight manner and between which are arranged tightly packed corrugated fins. Although these allow optimum heat transfer between the refrigerant flowing through the disks or tubes and the air flowing through the network of corrugated fins, they are inevitably subject to the precipitation of condensate and dust or dirt. This wet, contaminated heat transfer surface offers an ideal breeding ground for microorganisms, colonization of which can lead to the formation of undesirable odors. Moreover, in particular corrosion damage is promoted by the wet contamination.

To prevent the accumulation of water and dirt on a surface, the surface of an object is generally rendered hydrophobic. On account of the fact that spherical drops of water form on the surface as a result of the

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hydrophobic configuration thereof, and these drops then run off, these surfaces are fundamentally able to repel dirt and water. With a hydrophobic surface of the heat exchanger described, however, the water drops cannot  
5 run off, on account of the very closely packed corrugated fin structure. Instead, they remain in place between the adjacent, closely packed fins and gills. Therefore, the desired self-cleaning effect by the hydrophobic configuration is in fact prevented.  
10 Moreover, this usually leads to a decrease in the overall performance of the heat exchanger.

To solve this problem while maintaining the same design of heat exchanger, it is desirable for the heat  
15 transfer surfaces to be made hydrophilic.

The hydrophilicity of a substance is characterized, inter alia, by its polarity, a low interfacial tension with respect to water and good wettability with water,  
20 which results from the fact that the adhesion forces which act between the molecules of the same substance are high at an interface compared to the cohesion forces which act between the molecules of the same substance. If a surface can be successfully wetted, a  
25 drop of liquid forms a contact angle on said surface which is less than  $90^\circ$ , i.e. the liquid can spread out to a greater or lesser extent on the surface. Therefore, rendering a surface hydrophilic leads to the formation of a thin, continuous film of liquid. The  
30 continuous film of liquid allows the dust and dirt particles to flow off and therefore reduces long-term accumulation of dirt and dust. Since, moreover, the corrugated fin surface dries more quickly as a result of the relatively thin film of water which is formed,  
35 the colonization of microorganisms on the heat transfer surface is also reduced.

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By way of example, CN 13242732 has disclosed an aluminum heat exchanger which is provided with a layer which, inter alia, contains nanoparticles based on macromolecular surfactants and crosslinkable, unsaturated monomers and has corrosion-resistant and hydrophilic properties.

Furthermore, EP 1 154 042 A1 has disclosed a heat exchanger in which the heat exchanger surface, after acid cleaning, is provided with a chromium-containing or zirconium-containing conversion layer and a hydrophilic layer based on polymer which contains silicate particles with a diameter of between 5 and 1000 nm.

This type of coating means that compromises are generally required, and consequently, for example, optimum resistance to corrosion combined at the same time with a permanently hydrophilic surface to provide a self-cleaning action cannot be achieved with the same quality.

Consequently, the invention is based on the object of providing a heat exchanger of the above type, the heat transfer surfaces of which made from metal, in particular aluminum or aluminum compounds, are provided with a surface coating which represents an improvement on the prior art. Furthermore, it is intended to specify a process which is particularly suitable for this type of surface coating of the abovementioned heat exchanger.

With regard to the heat exchanger, the object is achieved, according to the invention, by a plurality of layers being applied to its heat transfer surfaces, with nanoparticles being used for the coating.

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In this context, the invention is based on the consideration that the design objectives of a long service life and an improved performance, which are pursued to equal extent for the heat exchanger, cannot  
5 be achieved, or at least cannot be achieved to a satisfactory extent, by a single layer. This applies in particular to design objectives which are actually divergent with respect to one another, namely for example on the one hand an optimized resistance to  
10 corrosion and on the other hand a hydrophilically configured surface. For example, a hydrophilic or water-attracting and therefore wet surface fundamentally promotes damage or destruction of materials by chemical or electrochemical reactions.  
15 Therefore, to avoid corrosion, it is fundamentally desirable to suppress contact between material and water by using a hydrophobic configuration. On the other hand, a hydrophilic surface is desirable for effective self-cleaning of the heat transfer surfaces,  
20 as described above, in order to promote the formation of a thin, continuous film of liquid which allows the dust and dirt particles to flow off.

To satisfy a plurality of, often contradictory, design  
25 objectives, therefore, a multiple coating is provided, each layer being suitable for its own specific property. Specifically, with one layer, defects in the layer can lead to the metal being exposed, and consequently this location in the metal, in particular  
30 in the case of a hydrophilic layer, i.e. a layer which attracts liquid, offers a suitable surface for attack in respect of corrosion damage. In the case of a plurality of layers, the probability that defects in the layer will lie directly above one another and  
35 expose the metal is reduced. This has a correspondingly beneficial effect with a view to reducing corrosion damage.

With regard to the materials used for the layers, tailored structures play an important role for the desired functions of the coating systems, such as for example the adhesion forces which are active between the molecules of different substances. The dimensions or sizes of individual components and mixtures play a crucial co-determining role in the formation of functional coatings. Particularly small particles, in particular with a size of a few millionths of a millimeter, are known as nanoparticles. The smallest nanoparticles are clusters of a few hundred molecules and are subject to the laws of quantum mechanics, whereas for larger nanoparticles the rules of traditional solid-state physics apply. Nanoparticles have a greatly reduced number of structural defects than larger particles of the same chemical composition. Therefore, on account of their geometric and material-specific properties, they offer a particularly wide and versatile spectrum of actions. For this reason, nanoparticles are used for the coating.

Nanoparticles can be produced, for example, by plasma processes, laser ablation, gas phase synthesis, sol-gel processes, spark erosion or crystallization, inter alia.

Nanoscale particles are distinguished by a particularly large surface area/volume ratio. Because the sticking force and bonding of the particles increases with an increase in surface area, layers produced in this way are generally particularly resistant to scratching and abrasion. As a result, the surface configured in this manner does not offer any surface for attack with respect to damage to the protective coating, with the result that, for example, corrosion damage can be minimized. By using nanoscale additives which are selected to have corresponding compositions, moreover, the resistance to corrosion is improved. On account of

their hydrophilicity and their relatively large surface area, these particles are hygroscopic. Consequently, their surface is wet and provides a thin film of liquid, which both allows the dirt and dust particles to flow off and also prevents the colonization of microorganisms as a result of the rapid drying of the thin film of liquid. Therefore, each layer of the heat exchanger preferably contains nanoparticles of different compositions.

To ensure improved performance and a longer service life of the heat exchanger, it is preferable for at least one layer to have corrosion-resistant properties and for at least one further layer to have hydrophilic and therefore self-cleaning properties.

In a particularly advantageous configuration, in particular for corrosion prevention reasons, it is preferable for a corrosion-resistant layer to be applied first of all, which is advantageously followed by a hydrophilic layer. To ensure that a particularly effective self-cleaning effect is achieved, the hydrophilic layer preferably forms the top layer of the multiple coating. The layer with hydrophilic properties advantageously has a wetting contact angle with water of less than or equal to  $60^\circ$ , preferably of less than or equal to  $40^\circ$ . The wetting contact angle is in this case determined by what is known as the sessile drop method, which represents an optical contact angle measurement for determining the wetting properties of solids.

In a particularly advantageous configuration of the heat transfer surfaces, it is expedient to use chromium-free, nontoxic additives for the surface coating. For this purpose, the nanoparticles used for the coating are preferably formed from organic and/or inorganic compounds of aluminum, silicon, boron and/or

transition metals, preferably from transition groups IV and V of the periodic system, and/or cerium dispersed and/or dissolved in inorganic and/or organic solvents.

- 5 For the heat exchanger to be used in air-conditioning systems, in particular in motor vehicles, for efficiency reasons it is expedient to provide a particularly thin coating which does not lead to any significant increase in volume and weight. Therefore,  
10 each layer thickness advantageously amounts to less than 1.5  $\mu\text{m}$  or equal to 1.5  $\mu\text{m}$ , preferably less than 1  $\mu\text{m}$  or equal to 1  $\mu\text{m}$ , and the total layer thickness amounts to less than 5  $\mu\text{m}$  or equal to 5  $\mu\text{m}$ .
- 15 With regard to the process for the surface treatment of heat exchangers, the abovementioned object is achieved by a plurality of layers being applied to a number of heat transfer surfaces made from metal, in particular from aluminum or aluminum compounds, with nanoparticles  
20 being used for the coating.

In this case, it is advantageous for nanoparticles of organic and/or inorganic compounds of aluminum, silicon, boron and/or transition metals, preferably  
25 from transition groups IV and V of the periodic system, and/or cerium dissolved and/or dispersed in inorganic and/or organic solvents to be used for coating.

It is advantageous for the layers to be applied by  
30 dipping, flooding or spraying, with the individual layers, in particular for particularly rapid layer build-up, being applied in direct succession, using what is known as the wet-in-wet technique, with just one drying operation.

35 In an alternative configuration of the process, the individual layers are preferably applied in separate treatment steps, in each case with intermediate drying.

The advantages achieved by the invention consist in particular in the fact that a multiple coating of heat transfer surfaces with nanoparticles used for the coating provides a heat exchanger which satisfies  
5 different and in some cases also divergent demands. The selected use of nanoscale particles of different materials achieves the desired functionality of the heat transfer surfaces. With this form of surface coating it is possible, for example, to improve the  
10 resistance to corrosion or the hardness and scratch proofing, and furthermore it is possible to produce self-cleaning and antimicrobial surfaces. For both an improved resistance to corrosion and at the same time also an improved self-cleaning effect brought about by  
15 rendering the heat transfer surface as hydrophilic, at least one corrosion-resistant layer and at least one further hydrophilic layer, in particular arranged thereon, are provided. Improved use and/or performance of the heat exchanger are achieved as a result of the  
20 abovementioned improved properties.

A heat exchanger, in particular an evaporator for air-conditioning systems in motor vehicles, having a double coating of its heat transfer surfaces made from  
25 aluminum substrate is provided as an exemplary embodiment. The nanoparticles for the respective layer are in this case produced using a sol-gel process.

Of course, depending on the desired profile of  
30 requirements, it is also possible for a multiple coating to be applied to the heat transfer surfaces, and of course the nanoparticles of different compositions for each layer can also be produced by processes other than the sol-gel process, such as for  
35 example by the plasma process, laser ablation, gas phase synthesis, spark erosion or crystallization, inter alia.



In the exemplary embodiment, a first corrosion-resistant layer, which is not hydrophilic, or the correspondingly configured base layer, is applied by dip coating in an organically modified inorganic sol-gel layer with water-based solvent. It is hardened by subsequent drying at a temperature in the range from 100 - 150°C for 10 minutes. The layer thickness produced is less than 1 µm. A further organically modified inorganic sol-gel layer with water-based solvent is applied by dip coating as the second layer or the covering layer. Its chemical composition differs from that of the layer below. The second layer or the covering layer is again hardened at 100 - 150°C for 10 minutes. Its surface has a hydrophilic character and has a wetting contact angle with water of less than 40°. This hydrophilicity is durable even under long-term action of condensation water, so that the contact angle is still below 40° even after condensation water exposure for over 1000 hours in accordance with the condensation water constant climate test in accordance with DIN 50017-KK. The total layer thickness of the layer structure comprising base layer and covering layer is at most 2 µm.

Therefore, the first layer or base layer ensures optimum resistance to corrosion, and the production of the functional hydrophilic covering layering improves the water run-off on the heat transfer surface. This helps dust and dirt to flow off the surface, and on account of the relatively thin film of water which is formed, faster drying of the surface is ensured. These self-cleaning and fast drying properties minimize the growth of microorganisms. All these factors improve the use properties and/or performance of heat exchangers having heat transfer surfaces which have been coated in this way.